Hyperbranched Poly(ester-enamine) from Spontaneous Amino-yne Click Reaction for Stabilization of Gold Nanoparticle Catalysts

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Abstract: Hyperbranched polymers have attracted much attention due to attractive properties and wide applications, such as drug controlled release, stimuli-responsive nano-objects, photosensitive materials and catalysts. Herein, a novel hyperbranched poly(ester-enamine) (hb-PEEa) was designed and synthesized via the spontaneous amino-yne click reaction of A_2 monomer (1, 3-bis(4-piperidyl)-propane or piperazine) and B_3 monomer (trimethylolpropanetripropiolate). By controlling monomer concentration, molar ratio and rate of addition, gelation during synthesis can be successfully avoided. The resultant hb-PEEa possesses favorable solubility in various organic solvents. Due to abundant alkynyl groups in termini, the hb-PEEa can be functionalized by different amino compounds or their derivates, which shows desirable potential in stabilization of metal nanoparticles. The amphiphilic PEG-hb-PEEa copolymer can be used as surfactant to stabilize Au nanopaticles (AuNPs) during reduction of $NaBH_4$ in aqueous solution. As a demonstration, the as-prepared PEG-hb-PEEa-supported AuNPs demonstrate good water solubility, high stability and remarkable catalytic activity for reduction of nitrobenzene compounds.

Keywords: hyperbranched polymers, amino-yne click reaction, nanocatalyst, reduction reaction

1. Introduction

Hyperbranched polymers (HBPs), as nano-sized highly-branched three-dimensional macromolecular architectures, have been broadly investigated and utilized in various applications including controlling drug delivery,[1-5] sensing,[6,7] and catalysis,[8-10] as well as materials science.[11-15] Because of the attractive properties and wide applications of HBPs, the development of new efficient and selective polymerizations to prepare functional HBPs is an invariably theme in polymer science. Since the concept of click chemistry was proposed in 2001, the click polymerizations had been widely utilized as a powerful technique in synthesis and modification of functional HBPs. For example, transition-metal catalyzed azide-alkyne click polymerizations (AACPs) have been widely used to synthesize hyperbranched polytriazoles.[16-21] In addition, the thiol-based click polymerizations have also been igniting great interesting in the preparation of sulfur-rich HBPs.[22-24] However, some aspects still need further enhancement in this field, i.e., the safety of azide monomers and the residue of metal catalysts in AACPs, the unpleasant smell and the limited types of thiol monomers in thiol-based click polymerizations.[25] As a result, it is challenging and very attractive to synthesize more novel functional HBPs using new click polymerizations in a mild condition.

In the past few years, Tang's group had developed several spontaneous click polymerizations including spontaneous thiol−yne click polymerization,[26] spontaneous amine−yne click polymerization,[27] and spontaneous phenol−yne click polymerization.[28] These amine−yne

polymerization demonstrated obvious advantages in a catalyst-free system with high efficiency, regioselectivity, 100% atom efficiency and mild conditions. Ni et al. synthesized polymer−doxorubicin prodrug via spontaneous amino−yne click reaction.[29] The prepared polymer shows good water solubility, biocompatibility, pH response and the potential in cancer therapy. Langer et al. synthesized the water-compatible β-aminoacrylate hydrogel platforms via the click polymerization between alkynoates and secondary amines.[30] However, merely reports are relative to the synthesis of functional HBPs via this click polymerization. In the meanwhile, multi-functional HPBs can be functional as templates to control the size, stability, and solubility of metal nanoparticles (metal NPs).[31-36] For the most part, HBPs-encapsulated metal NPs are prepared by sequestering metal ions within HBPs followed by chemical reduction to yield metal NPs. The particle size of metal NPs depends on the number of metal ions initially loaded into HBPs.[37,38] In addition, HBPs with highly branched and globular structure and multiple functional groups provide tremendous active sites and spatial constraint from aggregation of metal NPs, which are beneficial to improving efficiency in catalysis.[38-41] The terminal groups on the HBPs periphery can be tailored to control solubility of the hybrid nanocomposites to realize homogeneous catalysis of metal nanocomposites in water or organic solvents.

Herein, a series of novel hyperbranched poly(ester-enamine)s (hb-PEEa) with regional and stereo regular structure were designed and successfully synthesized by the spontaneous amino-yne click polymerization. As a demonstration, they were utilized as surfactant to synthesis AuNPs with remarkable catalytic activity for nitrobenzene compounds. First, the A_2 + B_3 monomers polymerization strategy including the A_2-type monomer (1, 3-bis(4-piperidyl)-propane or piperazine)

and the B_3-type monomer (trimethylolpropanetripropiolate) was chosen to synthesis HBPs. By controlling monomer concentration, molar ratio and rate of addition, the resultant hb-PEEa without gelation present good solubility in organic solvents. Abundant alkynyl groups on the termini of hb-PEEa can be further functionalized by different amino compounds, such as n-butylamine, diethyamine and NH_2-PEG (polyethylene glycol monomethyl ether). Second, the amphiphilic PEG-hb-PEEa synthesized through modification of NH_2-PEG containing a large number of amino and ester functions can capture metal ions and lead to the nucleation and growth of metal NPs. PEG-hb-PEEa are used as surfactant to synthesis colloidal AuNPs via in-situ reduction of Au ion using $NaBH_4$. The as-prepared PEG-hb-PEEa-supported AuNPs (AuNPs@PEG-hb-PEEa) show good water solubility and high stability, and demonstrate remarkable catalytic activity for reduction of nitrobenzene compounds. The synthesis of AuNPs@PEG-hb-PEEa provides a reference for the preparation of other functional metal nanocomposites.语义不通

2. Experimental section

2.1. Material characterization

All reagents and solvents were purchased from J.&K. Scientific Ltd (Beijing, China). Tetrahydrofuran (THF) was distilled through sodium under dry nitrogen before using. Other solvents were used without further purification. Reactions were followed with TLC (0.254 mm silica gel 60-F plates). Flash chromatography was carried out on silica gel of 200–300 mesh. All NMR spectra were obtained at ambient temperature using a Bruker-400 MHz spectrometer. Chemical shifts (δ) were reported as part per million (ppm) on the δ scale downfield from TMS. Multiplicities are reported as follows: *s* = singlet, *d* = doublet, *t* = triplet, *m* = multiplet. Fourier transform infrared spectroscopy (FT-IR) measurement was conducted on an FT-IR spectrophotometer (PerkinElmer, USA).

Transmission electron microscopy (TEM, FEI, Tecnai G2 F20) was performed at 200 kV. Samples for analysis were dispersed in alcohol and deposited on a holey carbon/Cu grid (200 mesh). UV-vis spectra were recorded using a spectrophotometer UV-2550 model (Shimadzu, Japan). Dynamic light scattering (DLS) measurements were made with a Zetasizer Nano-ZS (Malvern Instruments, UK). The samples were filtered using a microfilter (0.45 μm) prior to measurement. The number-average and weight-average molecular weight (M_n and M_w, respectively) and polydispersity index (PDI = M_w/M_n) were determined by gel-permeation chromatography (GPC) in THF on the basis of a polystyrene calibration.

2.2. Synthesis of trimethylolpropanetripropiolate (B_3 monomer)

Trimethylolpropane (40.25 g, 0.30 mol) and Propiolic acid (70.05 g, 1.0 mol) were added to the benzene (250 mL) with 5 mol% P-toluenesulfonic acid used as catalyst. A Dean-stark trap and a condenser were attached, and the reaction was protected under nitrogen. The mixture was heated to reflux for 24 h. Then the mixture was allowed to reach room temperature and diluted with EtOAc (250 mL), washed with 5 wt% Na_2CO_3 aqueous solution and brine and dried over anhydrous $MgSO_4$. The solvent was removed under reduced pressure and the purification of the reaction mixture by silica gel column chromatography eluting with EtOAc/petroleum (1/3) was performed to afford the product. IR (KBr, v, cm^{-1}): 3292.34, 3242.19, 2985.67, 2119.67, 1718.50, 1217.03, 983.65, 756.06, 707.84. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.19 (s, 6H), 2.93 (s, 3H), 1.56 (t, J = 8.0 Hz, 2H), 0.92 (t, J = 8.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 75.9, 74.2, 66.3, 40.8, 22.9, 7.4.

2.3. Synthesis of hyperbranched poly(ester-enamine) (hb-PEEa)

The polymerization of A_{2a} and B_3 monomers at the molar ratio of 1/1.2 is given below as an example. A single-necked 25 mL flask equipped with a magnetic stir bar was added 1, 3-bis(4-piperidyl)-propane (A_{2a} momomer) (42 mg, 0.2 mmol) and tetrahydrofuran (THF, 4 mL). Trimethylolpropanetripropiolate (B_3 monomer) (70 mg, 0.24 mmol) in 4 mL THF was injected into the above solution by syringe over 0.5 h. The mixture was stirred under dry nitrogen for 24 h at room temperature, and then the solution was poured slowly into an excess amount of hexane. The precipitate was collected and dried at room temperature under vacuum.

Characterization data for hb-PEEa-1 synthesized through the polymerization A_{2a} and B_3 monomers. IR (KBr, ν, cm^{-1}): 2926.67, 2845.77, 2117.78, 1688.44, 1609.11, 1455.11, 1237.33, 1123.77. ^1H NMR (400 MHz, $CDCl_3$) δ 7.39-7.36 (d, 1H), 4.64-4.61 (d, 1H), 4.21 (s, 0.8H), 4.08 (s, 2.1H), 3.50-3.47 (m, 2.1H), 2.94-2.91 (m, 2.4H), 1.71 (s, 2.8H), 1.54-1.17(m, 7.6H), 0.92 (s, 1.7H).

Characterization data for hb-PEEa-2 synthesized through the polymerization A_{2b} and B_3 monomers. IR (KBr, ν, cm^{-1}): 3253.33, 2968.67, 2113.11, 1697.78, 1602.89, 1448.89, 1349.33, 1224.89, 1142.44, 1004.00. ^1H NMR (400 MHz, $CDCl_3$) δ 7.40-7.29 (m, 1.0H), 4.73 (d, 1.0H), 4.21 (s, 1.4H), 4.09 (s, 2.0H), 3.31 (s, 4.0H), 2.95-2.92 (m, 0.7H), 1.80 (s, 0.6H), 1.58-1.51 (m, 1.1H), 1.28 (s, 0.5H), 0.95-0.88 (m, 2.0H).

2.4. Modification of hb-PEEa by amino-yne reaction

hb-PEEa-1 (50 mg, M_n = 8940 g mol^{-1}, PDI = 2.88) or hb-PEEa-2 (38 mg, M_n = 5080 g mol^{-1}, PDI = 3.02) dissolved in 4 mL THF. Amine compound in 2 mL THF (n-butylamine (7.3 mg) or diethyamine (7.3 mg) or NH_2-PEG (polyethylene glycolmonomethyl ether, M_n = 2000 g mol^{-1}) (200 mg) was injected via syringe. The mixture was stirred under dry nitrogen at room temperature for 12

h, and then added dropwise into hexane. The precipitate was collected by filtration and dried at room temperature under vacuum.

2.5. Preparation of AuNPs@ PEG-hb-PEEa

AuNPs@PEG-hb-PEEa was synthesized by mixing PEG-hb-PEEa-1 (10 mg, *Mn* = 78670 g mol^{-1}) or PEG-hb-PEEa-2 (10 mg, *Mn* = 30430 g mol^{-1}) and $HAuCl_4 \cdot 3H_2O$ (3 mg, 0.008 mmol) in deionized water (10 mL) under vigorous stirring for 1h. Then a freshly-prepared $NaBH_4$ (40 mg in 2 mL water) aqueous solution was added dropwise into the as-prepared solution. The obtained solution was continuously stirred for another 2 h. The AuNPs@PEG-hb-PEEa was purified by dialysis against a large volume of water (3 × 100 mL). The AuNPs@PEG-hb-PEEa was collected by freeze-drying.

2.6. Reduction of nitrobenzene compounds catalyzed by AuNPs@ PEG-hb-PEEa

The catalytic activity of AuNPs@PEG-hb-PEEa was examined by the reduction of nitrobenzene compounds in the presence of $NaBH_4$. In a typical experiment, an aqueous solution (3 mL) containing 0.9 μmol of p-nitrophenol and 0.09 mmol of $NaBH_4$ were added in a quartz cuvette. Then AuNPs@PEG-hb-PEEa catalyst in water (60 μl, 1 mg/mL) was introduced, and the reaction progress was detected by UV−vis spectroscopy. And the initial bright yellow solution gradually turned to colorless as the reaction progressed.

3. Results and discussion

The synthesis processes and structure of AuNPs@PEG-hb-PEEa are schematically shown in **Fig. 1**. The hb-PEEa are synthesized via the spontaneous amino-yne click polymerization of A_2 monomer (1,3-bis(4-piperidyl)-propane (A_{2a}) or piperazine (A_{2b})) and B_3 monomer

(trimethylolpropanetripropiolate), which can be further functionalized by NH_2-PEG. The structures of B_3 monomer were characterized by FT-IR and NMR spectroscopy (**Fig. S1**). The as-prepared amphiphilic PEG-hb-PEEa can effectively stabilize AuNPs. The resultant AuNPs@PEG-hb-PEEa composites efficiently catalyze reduction of nitrobenzene compounds in the presence of $NaBH_4$.

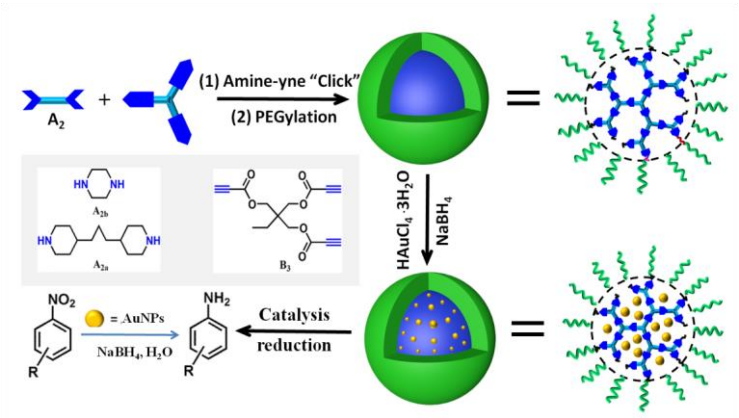

Fig. 1. Schematic synthesis process and structure of AuNPs@PEG-hb-PEEa and application in catalytic reduction of nitrobenzene compounds.

3.1. Synthesis and characterization of hb-PEEa

In this study, the A_2 + B_3 monomers polymerization strategy was applied to synthesis the HBPs. According to Flory's hypothesis, gelation is an intrinsic problem in an ideal A_2 + B_3 polymerization system.[42-45] During the polycondensation of A_2 with B_3 monomers, the gelated products take place when monomer solids are directly added or the addition of monomer solution is too quick. Besides the monomer concentration, other factors, such as slow addition of one monomer to another, monomer molar ratio, also account for avoiding gelation. Because of the high activity and efficiency of the amino-yne click reaction, the total monomer concentration should be lower and higher

monomer concentration lead to insoluble products. Throught slow addition approach to avoid any high local concentration, fully soluble hb-PEEa-1 (a2-a5, Table 1) could be synthesized by polymerization of A_{2a} and B_3 monomers at different molar ratios. As increasing the molar ratio of B_3 monomer, the average molecular weight (M_n and M_w) and polydispersity index (PDI) decreased accordingly. hb-PEEa-1 (a5) has M_n = 8940 g mol^{-1} and PDI = 2.88 at the molar ratio of 1.0/1.2. On the contrary, severe gelation quickly occurred at A_{2a}/B_3 molar ratio of 1.5/1.0 (equal molar concentration of functional groups) under the same polymerization conditions (a1). Furthermore, hb-PEEa-2 (a6) with M_n = 5080 g mol^{-1} and PDI = 3.02 was obtained via the polymerization of A_{2b} and B_3 monomer at the molar ratio of 1.0/1.2.

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Table 1. Polymerization condition for hyperbranched poly(ester-enamine) via spontaneous amino-yne click reaction.

Entry[a]	A_2/B_3 (molar ratio)	Mw^b [g mol^{-1}]	Mn^b [g mol^{-1}]	PDI[b]
a1[c]	1.5:1.0	insoluble	insoluble	insoluble
a2[d]	1.0:1.0	36,270	6,990	5.19
a3	1.0:1.0	197,610	33,280	5.94
a4	1.0:1.1	80,580	25,550	3.16
a5	1.0:1.2	25,780	8,940	2.88
a6	1.0:1.2	15,360	5,080	3.02

[a]Carried out in THF under nitrogen for 24 h; monomer concentration (A_2 = 20 mM); all yields over 90% by precipitation from hexane; a1-a5 from the polymerization between A_{2a} and B_3, a6 from the reaction of A_{2b} and B_3 monomers. [b]Molecular weight (g mol $^{-1}$) determined by gel-permeation chromatography (GPC) in THF on the basis of a polystyrene calibration: M_w = weight-average molecular weight, M_n = number-average molecular weight, PDI = M_w /M_n. [c]Molecular weight could not be obtained because the polymer was not soluble in common solvents. [d]Reaction time is for 12 h.

By optimizing the polymerization conditions, hb-PEEa can be rapidly and effectively synthesized. The resultant hb-PEEa are soluble in common organic solvents such as dichloromethane, acetone, ethanol, and tetrahydrofuran. The molecular structure of hb-PEEa was identified by FT-IR and NMR spectroscopy. By analyzing the FT-IR spectra of A_{2a} monomer, B_3 monomer, and hb-PEEa-1 (Fig. S2a), the N−H vibration of A_{2a} monomer occur at 3190.0 cm^{-1}, which disappears completely after polymerization. The characteristic absorptions of B_3 monomer at 3242.2 and 2119.7 cm^{-1} can be assigned to the ≡C-H and C≡C stretching vibrations, which weak in the hb-PEEa-1. The key absorption of new C=C is at 1609.1 cm^{-1} in the hb-PEEa-1. These results reveal the occurrence of the polymerization and there are many unreacted alkynyl groups in its periphery. From the ^{1}H NMR spectrum (Fig. 2a), two new peaks (**l** and **m**) assigned to the resonances of the vinylene protons appear at 7.4 and 4.6 ppm in the spectra of hb-PEEa-1. The ≡C-H (**n**) of B_3 monomer at 2.9 ppm was shifted to 4.21 ppm in hb-PEEa-1. And the intensity of the alkynyl units becomes weaker after polymerization, which also indicates alkynyl units as terminal units. Furthermore, the hb-PEEa-1 was investigated by ^{13}C NMR spectroscopy (Fig. S3). There are some characteristic signals at 169.8, 152.7, 151.2 and 83.4 ppm, which represent the carbon atoms of the ester carbonyl units and the vinylene groups, respectively. The molecular structure of hb-PEEa-2 was also characterised by FT-IR (Fig. S2b) and NMR (Fig. 2b and S4). The analysis results showed that hb-PEEas could be successfully synthesized by the amino-yne click reaction of A_2 and B_3 monomers.

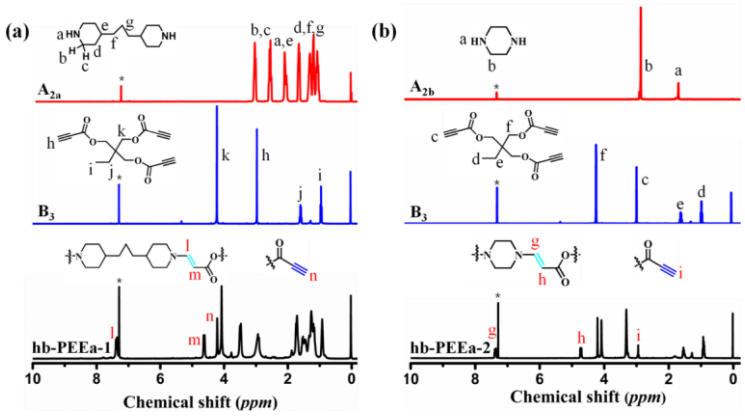

Fig. 2. ^{1}H NMR spectra in $CDCl_3$: (a) A_{2a}, B_3 and hb-PEEa-1, (b) A_{2b}, B_3 and hb-PEEa-2.

3.2. Modification of hb-PEEa by amino-yne click reaction

According to structure analysis of hb-PEEa, there are a large number of unreacted alkynyl groups in the periphery of hb-PEEa, which can be further functionalized via amino-yne reaction. By simply mixing the hb-PEEa and the different amines such as n-butylamine, diethyamine and NH_2-PEG (polyethylene glycolmonomethyl ether, M_n = 2000 g mol^{-1}) in THF at room temperature for 12 h, the quantitative reaction of the terminal alkynyl groups was observed by FT-IR and ^{1}H NMR spectroscopy. The vibration of ≡C−H completely disappear and the absorption of C=C enhance after post-polymerization in the FT-IR spectrum (Fig. S5). By analyzing the ^{1}H NMR spectra (Fig. S6 and S7), we can observe some peaks of new vinylene protons with the disappearance of the alkynyl groups. As indicated by the GPC measurement, the M_n of PEG-hb-PEEa-1 (78670 g mol^{-1}) and PEG-hb-PEEa-2 (30430 g mol^{-1}) is enhanced compared with that of hb-PEEa-1 (8940 g mol^{-1}) and hb-PEEa-2 (5080 g mol^{-1}), respectively, Meanwhile, the PEG-modified hb-PEEa (PEG-hb-PEEa) are soluble in water in contrast to hb-PEEa.

3.3. Preparation and characterization of AuNPs@ PEG-hb-PEEa

The amphiphilic PEG-hb-PEEa contain a large number of amino and ester functions, which can be used to capture heavy metal ions, guide the nucleation and growth of metal NPs, and enhance the interaction between support and loaded metal NPs. Therefore, PEG-hb-PEEa could be used as organic templates to stabilize metal NPs in water. AuNPs@PEG-hb-PEEa was synthesized by mixing PEG-hb-PEEa and $HAuCl_4 \cdot 3H_2O$ in deionized water under vigorous stirring. During the process, Au(III) ions were sequestered into PEG-hb-PEEa. A freshly prepared $NaBH_4$ solution was then added dropwise into the as-prepared solution. Then Au (III) ions were reduced by $NaBH_4$, and the Au(0) atoms gathered together leading to the formation of stable AuNPs inside the PEG-hb-PEEa. The color of the solution gradually becomes purple with the formation of AuNPs. The size and morphology of AuNPs were determined by typical transmission electron microscope (TEM) (Fig. 3a and 3b). The DLS analysis displays the hydrodynamic behavior, and AuNPs@PEG-hb-PEEa has a narrow dispersion in aqueous solution by the DLS measurement (Fig 3c). Moreover, UV−vis spectra reveals the plasmonic properties of Au NPs, with the change of the surface plasmon band (SPB) along with the variety of sizes. The surface plasmon band (SPB) was observed at 531 nm for AuNPs@PEG-hb-PEEa-1, 524 nm for AuNPs@PEG-hb-PEEa-2 (Fig. 3d). Furthermore, we do not see the aggregation and color change in aqueous solution under ambient conditions for several weeks, showing AuNPs@PEG-hb-PEEa have good stability. The final content of gold is 1.2 wt% (AuNPs@PEG-hb-PEEa-1) and 1.8 wt% (AuNPs@PEG-hb-PEEa-2) from ICP analysis, respectively. These results suggest promising applications of AuNPs@PEG-hb-PEEa in aqueous media.

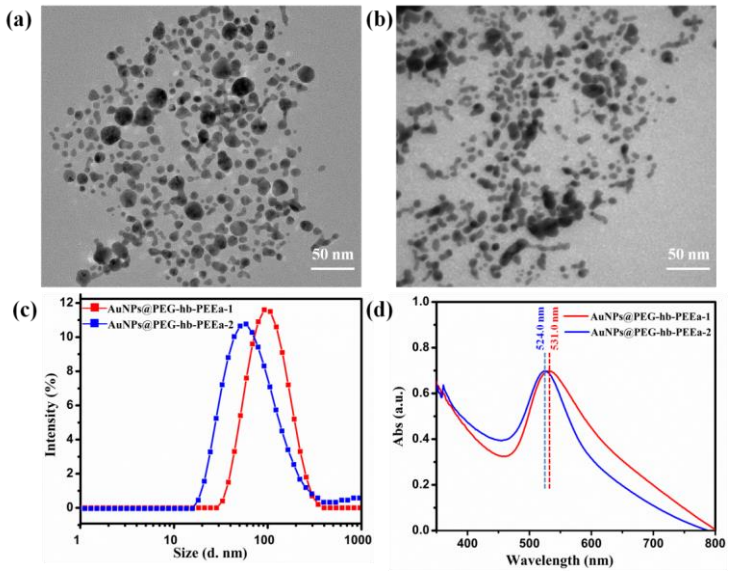

Fig. 3. TEM images of Au NPs: (a) AuNPs@PEG-hb-PEEa-1 and (b) AuNPs@PEG-hb-PEEa-2; (c) DLS size distribution; (d) UV-vis spectrum.

3.4. Catalytic reduction of nitrobenzene compounds

Because nitrobenzene compounds are toxic and hazardous pollutants in industrial and agricultural waste water, especially p-nitrophenol (4-NP). They have high stability and low solubility in water, so their degradation in nature has always been difficult and challenging.[46, 47] In general, 4-NP reduction in the presence of $NaBH_4$ is a versatile reaction to evaluate the catalytic activity of various metal NPs, and this reaction can also be readily monitored by UV−vis spectroscopy. The as-prepared AuNPs@PEG-hb-PEEa have good water solubility and high stability, and its application in catalysis was explored. The reduction of 4-NP in the excess presence of $NaBH_4$ was chosen as a model reaction to evaluate the catalytic activity of AuNPs@PEG-hb-PEEa and monitored dynamically by UV-Vis spectra. As a control experiment, the reaction did not occur when using only PEG-hb-PEEa

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as catalyst. The intensity of the absorption peak at 400 nm, a characteristic peak of 4-NP and $NaBH_4$, remains almost unchanged in the presence of PEG-hb-PEEa at a prolonged period. This means that the PEG-hb-PEEa alone does not have catalytic activity. By adding AuNPs@PEG-hb-PEEa as a catalyst, the reduction was initiated immediately, showing the rapid decrease of the absorption at 400 nm and the related increase of the characteristic peak of p-aminophenol (Fig. 4a and 4b). And the color of the solution gradually changed from bright yellow to colorless (Fig. 4c, inset image). Since $NaBH_4$ was used in excess compared to the 4-NP in the system, the reduction of 4-NP can be considered as a pseudo-first order reaction to evaluate the kinetic reaction rate of the catalytic reaction. Herein, Fig. 4d show a linear correlation of ln(At/A0) versus time at any instant. K_{app} (the apparent rate constant) is 12.80×10^{-3} s^{-1} for AuNPs@PEG-hb-PEEa-1 and 21.78×10^{-3} s^{-1} for AuNPs@PEG-hb-PEEa-2. In order to ensure the universal applicability of AuNPs@PEG-hb-PEEa, other nitrobenzene compounds with different substituent groups were also considered (Fig. S8). The results illustrate that the AuNPs@PEG-hb-PEEa exhibit efficient catalytic activity for the reduction of other nitrobenzene compounds. The substituents of the nitro para position have a great influence on the rate of reduction reaction, and the electron withdrawing groups (Br or F) have a faster reaction, compared with the electron donating groups.[48]

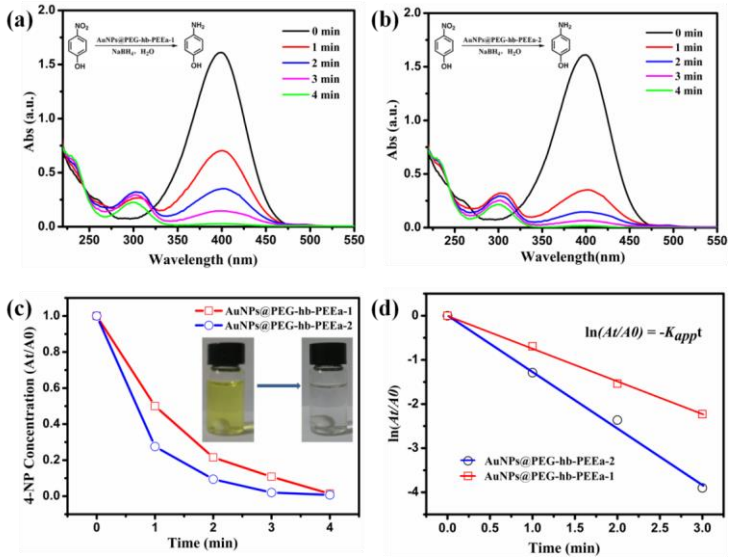

Fig. 4. Time-dependent UV-vis spectra of the reduction of p-nitrophenol (0.9 μmol) and 0.09 mmol $NaBH_4$ catalyzed by 60 μL AuNPs@PEG-hb-PEEa solution (1 mg/mL), (a) AuNPs@PEG-hb-PEEa-1 solution; (b) AuNPs@PEG-hb-PEEa-2 solution; (c) At/A0 as a function of reaction time, Inset images: typical optical images of reaction mixtures at 0 and 4 min; (d) linear relationship of ln(At/A0) as a function of time.

4. Conclusion

In summary, a series of novel hyperbranched Poly(ester-enamine)s were successfully synthesized via the spontaneous amino-yne click polymerization of A_2 monomer (1,3-bis(4-piperidyl)-propane or piperazine) and B_3 monomer (trimethylolpropanetripropiolate). By optimizing the polymerization conditions, gelation can be successfully avoided and the resultant hb-PEEa show good solubility in common organic solvents. The resultant hb-PEEa can be further functionalized via amine−yne click

reactions. PEG-modified hb-PEEa (PEG-hb-PEEa) can be used as surfactant in the stabilization of Au NPs in water. The as-prepared AuNPs@PEG-hb-PEEa show good catalytic activity for efficient reduction of nitrobenzene compounds under mild conditions.

Conflict of interest

The authors declare no competing financial interest.

Supporting Information

Supporting Information is available from the Online Library or from the author.

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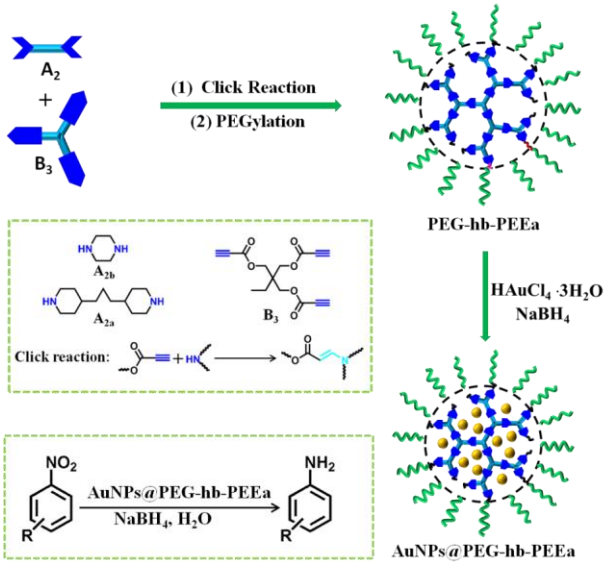
Highlights

- Rapid and efficient synthesis of hyperbranched poly(ester-enamine) via the spontaneous amino-yne click reaction.
- Gelation was successfully avoided by controlling polymerization conditions.
- The nanocatalyst AuNPs@PEG-hb-PEEa exhibit good catalytic activity toward the reduction of nitrobenzene compounds.

TOC Figure



Novel hyperbranched poly(ester-enamine)s (hb-PEEa) were effectively synthesized by the spontaneous amino-yne click reaction of A_2 + B_3 monomers. The amphiphilic PEG-hb-PEEa were used as surfactant for stabilization of Au nanoparticles (AuNPs). The PEG-hb-PEEa-supported AuNPs composites (AuNPs@PEG-hb-PEEa) show remarkable catalytic activity for catalytic reduction of nitrobenzene compounds.